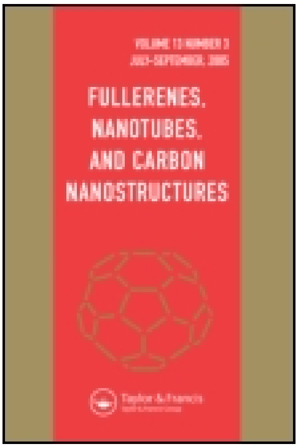

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Raman Study of the Pressure-Induced Charge Transfer Transition in the Neutral Donor-Acceptor Complexes $\{Ni(nPr_2dtc)_2\}(C_{60})_2$ and $\{Cu(nPr_2dtc)_2\}(C_{60})_2$

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Raman spectra of the neutral state donor–acceptor complexes $\{Ni(nPr_2dtc)_2\}(C_{60})_2$ *and* $\{Cu(nPr_2dtc)_2\}(C_{60})_2$ *were measured at pressures up to 7 GPa and at room temperature. The splitting of the* $A_g(2)$ *PP-mode of* C_{60} *at* $\sim$*0.7 GPa is accompanied with redistribution of intensity from the high frequency component to the low frequency one that dominates the spectra at* $P > 2$ *GPa. Thus, the PP-mode shows an overall softening by* $\sim$*6 cm*$^{-1}$ *near 2 GPa, while the pressure dependence is reversible with some hysteresis. The observed peculiarities are associated with the pressure-induced charge transfer of one electron from the organic donor to the fullerene acceptor.*

Keywords Fullerene, charge transfer, pressure, Raman spectra

Introduction

Donor-acceptor complexes of fullerenes are extensively studied in connection with their structure, optical and magnetic properties (1). Fullerene complexes were synthesized with different classes of donor molecules, such as aromatic hydrocarbons, tetrathiafulvalenes, amines, metalloporphyrins, metallocenes and others. Various organic donors form a wide family of compounds with fullerenes, which have both neutral and ionic ground states. The behavior of the donor-acceptor complexes of fullerenes at high pressure is of great interest due to possible formation of dimers and/or zig-zag polymeric chains between the fullerene molecules similar to those of the pristine C_{60} (2). Another possibility is the pressure-induced charge-transfer between the organic donor and fullerene acceptor in the initially neutral donor-acceptor complexes. In the present paper we report the first results of the Raman study of the pressure-induced charge transfer in the neutral donor-acceptor complexes $\{Ni(nPr_2dtc)2\}(C_{60})_2$ and $\{Cu(nPr_2dtc)_2\}(C_{60})_2$.

Experimental Details

The ability of $M(R_2dtc)x$ donors to co-crystallize with C_{60} as well as the composition of the complexes depend on the metal (M) and the length of the alkyl substituents (R). The samples of the donor-acceptor complexes of C_{60}, $\{Ni(nPr_2dtc)_2\}(C_{60})_2$ and

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$\{Cu(nPr_2dtc)_2\}(C_{60})_2$ were obtained by evaporation of solutions containing fullerenes and the corresponding donors. Raman spectra from small pieces of the $\{Ni(nPr_2dtc)_2\})(C_{60})_2$ and $\{Cu(nPr_2dtc)_2\}(C_{60})_2$ complexes of ∼30 μm in diameter were recorded *in-situ* in the back-scattering geometry using a micro-Raman setup composed of a spectrograph Acton SpectraPro-2500i and CCD Pixis2K detector system cooled down to −75°C. The 514.5 nm line of an Ar^+ laser was focused on the sample by means of a fiber and an Olympus 50× objective in a spot of ∼10 µm diameter; the scattered laser line was suppressed by a super-notch filter with suppression efficiency OD = 6 and band width ∼160 cm^{-1}; and the beam intensity before the diamond anvil cell was lower than ∼2 mW. The laser intensity used in our experiments does not result in any detectable changes in the Raman spectra of material even at very long exposition times. Measurements of the Raman spectra at high pressure were carried out using a diamond-anvil cell (DAC) of Mao-Bell type. To avoid oxidation of complexes in common liquids, the fluorinert FC70/FC77 1/1 mixture was used as pressure transmitting medium while the ruby fluorescence technique was used for pressure calibration.

Results and Discussion

Figure 1a shows the Raman spectra of the $\{Cu(nPr_2dtc)_2\}(C_{60})_2$ at pressures up to 6 GPa in the region of $A_g(2)$ pentagon-pinch (PP) mode of C_{60} recorded upon pressure increase.

The phonon modes of the C_{60} molecule dominate in the spectra whereas the modes of the donor molecule are not represented, most likely due to their relatively small cross-section of Raman scattering. When pressure increases, the phonon frequencies increase while the absolute intensities of Raman scattering and the relative intensity of the most intense PP-mode decrease. In addition, the PP-mode splits near ∼0.9 GPa and considerably broadens at $P > 2$ GPa. Figure 1b shows the Raman spectra of $\{Cu(nPr_2dtc)_2\}(C_{60})_2$ recorded upon pressure release. The pressure behavior of Raman bands is generally reversible despite some increase in the background. The Raman spectra of the $\{Ni(nPr_2dtc)_2\}(C_{60})_2$ at high pressure up to 7 GPa show similar peculiarities. Figure 2 depicts the pressure dependence of the Raman band frequencies in the region of the PP-mode of the $\{Ni(nPr_2dtc)_2\}(C_{60})_2$ for pressures up to 7 GPa.

Open (closed) symbols show data for the increase (decrease) of pressure. The pressure dependence of the PP-mode frequency is reversible with some hysteresis in the pressure region 0–3 GPa (shaded area in Figure 2). In this pressure region, the PP-mode softens; initially the PP-mode splits into two components at ∼0.7 GPa that differ in frequencies by ∼6 cm^{-1}.

Figure 3 shows in more details the pressure dependence of the PP-mode of the $\{Ni(nPr_2dtc)_2\}(C_{60})_2$ in the pressure region up to 4 GPa (shaded ring area in Figure 2). Closed circles in Figure 3 represent data recorded upon pressure increase, while the closed squares represent data recorded upon pressure release. Open circles show the split component upon pressure increase; open squares, upon pressure release, while the lines are guide for the eye. The insert in Figure 3 shows the variation of the intensities of the split components. When pressure increases, the intensity of the high frequency component decreases and this band disappears at ∼2 GPa, while the intensity of the low frequency component increases and dominates the spectra at $P>2$ GPa.

The softening of the $A_g(2)$ PP-mode in the pristine fullerene is related to the formation of dimers or polymeric networks of various dimensionalities (2). The value of the softening increases with the increase in the number of intermolecular links (the number of the

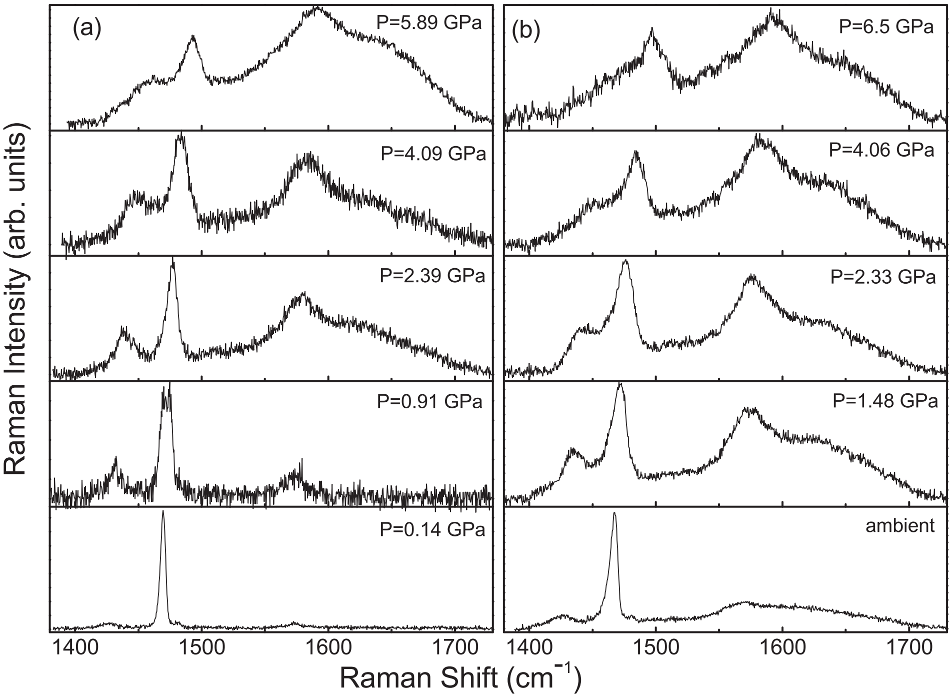

Figure 1. Raman spectra of the $\{Cu(nPr_2dtc)_2\}(C_{60})_2$ in the region of the PP-mode at pressures up to 7 GPa and room temperature. Left panel – upstroke measurements; right panel – downstroke measurements.

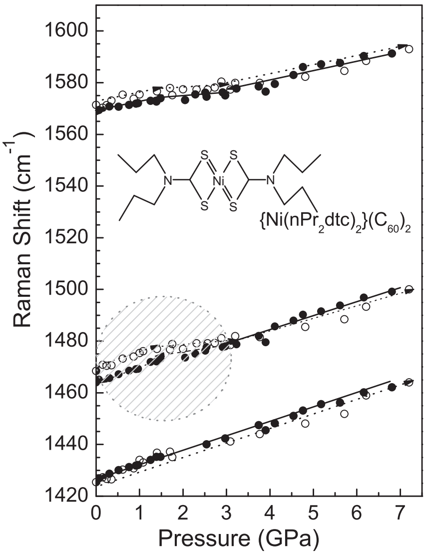

Figure 2. Pressure dependence of the phonon frequencies of the $\{Ni(nPr_2dtc)_2\}(C_{60})_2$. Open symbols – upstroke measurements; closed symbols – downstroke measurements. Shaded area shows the pressure region where the charge transfer takes place, while lines are guide for the eye.

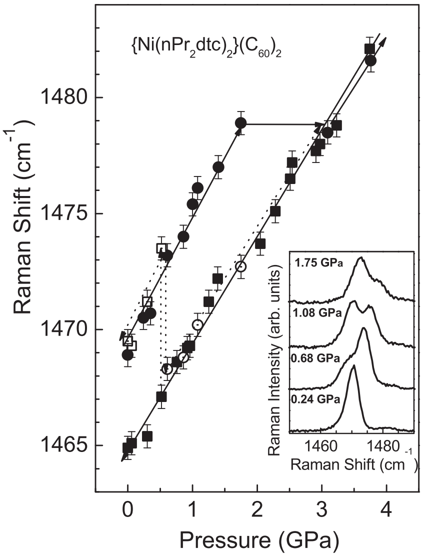

Figure 3. Pressure dependence of the PP-mode frequency of the {Ni(nPr$_2$dtc)$_2$}(C$_{60}$)$_2$ in the initial pressure region. Closed circles correspond to pressure increase, while closed squares to pressure decrease. Open symbols refer to the split component. Lines are guides for the eye. Inset: The split PP-mode in the Raman spectra of the {Ni(nPr$_2$dtc)$_2$}(C$_{60}$)$_2$ in the initial stage of the pressure increase.

sp^3-like coordinated carbon atoms in the fullerene molecule); the minimum softening is ~5 cm^{-1} in the case of C$_{60}$ dimers (3). The pressure-induced polymerization is accompanied with the irreversible changes in the Raman spectra related to the deformation of the fullerene molecular cage that results in the symmetry lowering and splitting of numerous degenerate molecular modes (2,4). On the other hand, the charge transfer in the intercalated by alkali, alkaline-earth and rare-earth metals fullerene leads also to the softening of the PP-mode. For example, the transfer of one electron from Rb to C$_{60}$ in the RbC$_{60}$ compound results in the softening of the PP-mode by 7cm^{-1} (5). Similarly, the formation of the (C$_{60}$$^{\bullet-}$) radical anions (–1 is the charge of C$_{60}$) in the ionic complex (DMI$^+$)$_3$·(C$_{60}$$^{\bullet-}$)·(I$^-$)$_2$ of fullerene (6) also results in softening of PP-mode by ~6 cm^{-1}. The softening of PP-mode due to the charge transfer differs from that of related to fullerene polymerization because it is not accompanied with symmetry lowering and splitting of degenerate modes (2,4). Thus, the reversible softening of the PP-mode and the absence of other degenerate mode splitting in the donor-acceptor complexes of C$_{60}$ may be the main indication of a possible pressure-induced charge transfer. It is important to note that the most impressive feature in the pressure behavior of the {Cu(nPr$_2$dtc)$_2$}(C$_{60}$)$_2$ and the {Ni(nPr$_2$dtc)$_2$}(C$_{60}$)$_2$ complexes is the splitting of the non-degenerate PP-mode and its softening, contrary to the absence of degenerate C$_{60}$ modes splitting, as well as the reversible pressure behavior of Raman modes. The observed peculiarities, in our opinion, are related to the presence of two C$_{60}$ molecules in complexes that are located in different positions; one of them is closer to the donor and is preferable for the charge transfer. Thus, the appearance of the split component of the PP-mode is related to the transfer of one electron from the donor to the closer located C$_{60}$ molecule whereas the second C$_{60}$ molecule remains in the neutral state. The pressure-dependent variation of the split component intensities may be an indication of a gradual pressure-induced charge transfer. Finally, we believe that the obtained data are an undoubted indication of the pressure-induced charge-transfer in the neutral state donor-acceptor complexes $\{Cu(nPr_2dtc)_2\}(C_{60})_2$ and $\{Ni(nPr_2dtc)_2\}(C_{60})_2$. As a next step, we are planning to undertake an X-ray diffraction study of these complexes at high pressure to clarify the structural aspects of the observed, by Raman scattering, pressure-induced charge-transfer transition.

Acknowledgments

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